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Spectrophotometric Determination of Pd(II) Using 4-Methyl Benzaldehyde Oxime

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Spectrophotometric method has been developed for the determination of palladium(II) using 4-methyl benzaldehyde oxime as a reagent. The reagent reacts with Pd(II) giving yellow coloured complex which can be quantitatively extracted in butanol at pH 6.0. Molar absorptivity at 415 nm is 0.8857×10^2 L mol^{-1} cm^{-1}. Beer's law is obeyed in the range of 1 to 12 ppm. The present method has been used for analysis of Pd(II) in silver alloy and palladium catalysts.

Key Words: Spectrophotometric determination, Pd(II), 4-Methyl benzaldehyde oxime.

INTRODUCTION

Oxime[1] is one of the important classes of analytical reagents widely employed for the spectrophotometric determination of metal ions. The oxime group has two donor atoms N and O and coordinates to a metal atom through either or both, thus acting as unidentate or bidentate ligand respectively. Survey of literature[2–4] reveals that due to versatility of these oximes to form complexes as well as their reactions like nitrosation, formation of heterocycles and nitrimines, they have been studied with great interest. Herein, the determination of palladium(II) using 4-methylbenzaldehyde oxime (4-MBO) as a reagent is reported.

EXPERIMENTAL

The absorption measurements were made on a Shimadzu UV-Vis 2100 spectrophotometer with 1 cm quartz cells and the digital pH-meter Li-120 model of Elico Pvt. Ltd. was used for pH measurement study. The chemicals used were of analytical reagent grade. Stock solution of palladium was prepared by dissolving $PdCl_2$ (Merck) in double distilled water containing few drops of concentrated hydrochloric acid and standardized by known method[5]. The reagent 4-methylbenzaldehyde oxime was prepared as reported in the literature[5].

Procedure for extraction

1.0 mL of aqueous solution containing 0.1 mg of palladium metal and 1 mL of reagent were mixed in a 50 mL beaker. The pH of the solution was adjusted to 6.0

keeping the volume 10 mL. The solution was transferred to a 100 mL separating funnel. The beaker was washed twice with *n*-butanol and transferred. The two phases were shaken for 2 min and allowed to separate. The organic phase was collected in a 10 mL measuring flask and made up to the mark with organic solvent, if required. After separation of the two phases, the pH of the aqueous phase was measured and the Pd(II) in each phase was determined by isonitrosoacetophenone (HINAP) method[5].

Procedure for determination of palladium in silver alloy

0.5 gm of alloy was dissolved in 10 mL nitric acid (1 : 1) and the solution was evaporated to dryness. The residue was dissolved in 10–15 mL of distilled water and silver was precipitated as AgBr by adding KBr solution. The precipitate was removed by filtration, washed with dilute nitric acid and finally with water. The filtrate was concentrated to 2–3 mL and diluted to 25 mL with water. An aliquot (1 mL) of this solution was used for the estimation of palladium by the procedure as described above.

Procedure for determination of palladium in catalysts

1. 0.1 g of palladium charcoal was taken in a silica combustion tube and incinerated for 8 h to ash the carbon completely. The sample was treated with 5 mL of formic acid and dried on a hot plate. The resulting compound was dissolved in 6 M HCl and 2 M nitric acid, and then diluted to 100 mL with distilled water.
2. 0.1 g of Pd-calcium carbonate catalyst was taken in a beaker, treated with aqua regia and evaporated to dryness. The residue was leached with water. Hydrochloric acid was added and diluted to 100 mL with distilled water. Aliquots of these samples were analyzed by the proposed method and the results obtained were found to be in good agreement with the standard mehod.

RESULTS AND DISCUSSION

4-Methyl benzaldehyde oxime (4-MBO) forms yellow coloured complex with Pd(II), which can be extracted into organic phase. The extraction of Pd(II) from an aqueous phase by 4-MBO in *n*-butanol is studied over a wide range of experimental conditions. The results of various studies are discussed below:

Effect of pH on the extraction of Pd(II): The extraction of palladium with 4-MBO has been studied over the pH range 1–10. It was observed that the % E of Pd(II) with 4-MBO was maximum between the pH range 5.8–6.2 and further the extraction of the complex decreases.

Absorption spectrum of Pd(II): 4-Methyl benzaldehyde oxime in *n*-butanol shows the maximum absorption at 415 nm. The absorption due to the reagent at this wavelength is nearly negligible. Hence 415 nm was selected for the absorbance measurement in spectrophotometric determination of palladium against the reagent blank.

Calibration curve: A calibration plot of absorbance against concentration of Pd(II) gives linear and reproducible graph in the concentration range 1–12 ppm of palladium indicating that the Beer's law is obeyed in this range (Fig. 1). The

molar absorptivity and Sandell's sensitivity were calculated to be 0.8857×10^2 L mol^{-1} cm^{-1} and 0.08857 μg cm^{-2}, respectively.

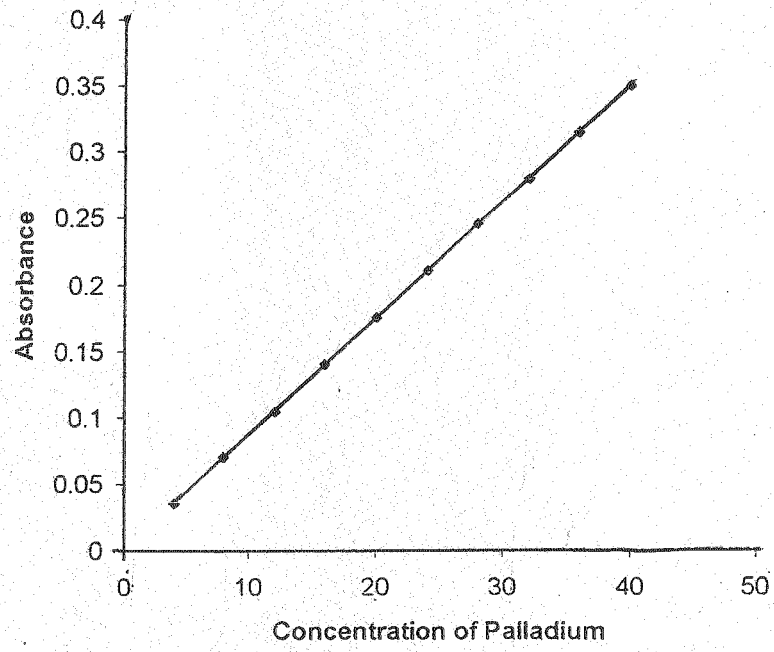

Fig. 1. Calibration plot of Pd(II) with 4-methyl benzaldehyde oxime

Nature of extracted species: The composition of extracted species was determined by Job's continuous variation method, slope ratio method (Fig. 2), and mole ratio method. It shows that the composition of Pd(II) : 4-methylbenzaldehyde oxime complex is 1 : 2.

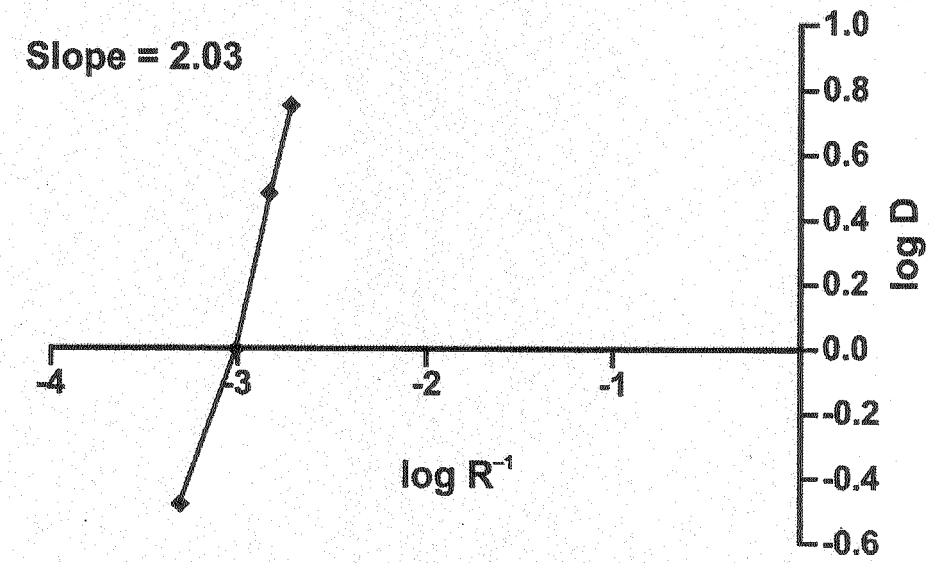

Fig. 2. Stoichiometric ratio of metal to reagent complex of Pd(II) with 4-MBO in *n*-Butanol from aqueous media

Effect of foreign ions: The effect of other ions present (Tables 1 and 2) in various amounts does not interfere in the spectrophotometric determination of 100 μg of palladium. The ions which show interference in the spectrophotometric determination of palladium was overcome by using appropriate masking agents.

TABLE-1
STUDY OF INTERFERENCE OF ION ON ABSORBANCE OF Pd(II) : 4-MBO

Total amount of Pd taken : 320 μg
Aqueous phase : 10.0 mL containing 2.0 mL of 1% 4-MBO in ethanol
Organic phase : 10.0 mL (2 × 5) of *n*-butanol
Wavelength : 415 nm pH : 6.0

S.No.	Ion	Amount added (mg)	Absorbance at 415 nm	S.No.	Ion	Amount added (mg)	Absorbance at 415 nm
1	—	—	0.560	11	$S_2O_3^{2-}$	9.5	0.560
2	Cl^-	25.0	0.560	12	NO_2	12.5	0.560
3	Br^-	22.0	0.560	13	NO_3	11.0	0.560
4	I^-	19.5	0.560	14	PO_4^{3-}	8.5	0.560
5	F^-	18.5	0.560	15	$P_2O_7^{2-}$	8.5	0.560
6	ClO_3^-	12.5	0.560	16	CN^-	11.5	0.560
7	BrO_3^-	12.5	0.560	17	CNS^-	6.5	0.560
8	IO_3^-	15.0	0.560	18	ClO_4^-	11.0	0.560
9	SO_3^{2-}	11.0	0.560	19	Thiourea	12.5	0.560
10	SO_4^{2-}	11.0	0.560	20	Oxalate	15.0	0.560

TABLE-2
EFFECT OF INTERFERENCE OF SOME DIVALENT IONS ON ABSORBANCE OF Pd(II): 4-MBO COMPLEX IN *n*-BUTANOL

Total amount of palladium taken : 320 μg
Aqueous phase : 10.0 mL containing 2.0 mL of 4-MBO (1%) in ethanol
Organic phase : 10.0 mL (2 × 5) of *n*-butanol
Wavelength : 415 nm pH : 6.0

S.No.	Metal	Amount added (mg)	Absorbance at 415 nm	S.No.	Metal	Amount added (mg)	Absorbance at 415 nm
1	—	—	0.560	11	Pb^{2+}	8.0	0.560
2	Li^+	12.0	0.560	12	Hg^{2+}	10.0	0.560
3	Na^+	18.0	0.560	13	Bi^{2+}	8.0	0.560
4	K^+	8.0	0.560	14	Cu^{2+}	15.0	0.560
5	Mg^{2+}	8.0	0.560	15	Cr^{3+}	8.0	0.560
6	Ca^{2+}	10.0	0.560	16	Sn^{2+}	10.0	0.560
7	Ba^{2+}	15.0	0.560	17	Fe^{2+}	10.0	0.560
8	Sr^{2+}	15.0	0.560	18	Zr^{2+}	10.0	0.560
9	Al^{3+}	18.0	0.560	19	Sb^{2+}	9.0	0.560
10	Be^{2+}	10.0	0.560				

Precision and accuracy: The precision and accuracy of the spectrophotometric method have been studied by analyzing five solutions each containing 100 μg of palladium (Table-3).

Applications: The proposed method has been applied to determine palladium in binary mixtures, silver alloy and palladium catalysts. The results of the analysis are comparable with dimethyl glyoxime method (Tables 4 and 5).

TABLE-3
PRECISION AND ACCURACY OF THE METHOD

Aqueous phase : 200 μg of Pd(II) + 1.0 mL of 4-MBO (1%) in ethanol
Organic phase : 10.0 mL (2 × 5) of *n*-Butanol
Wavelength : 415 nm
pH : 6.0

Obs. No.	Absorbance (nm)	Amt. of Pd(II) (mg)	$\overline{X}$	$D = \lvert X_i - \overline{X} \rvert$	$D^2 = (X_i - \overline{X})^2$
1	0.175	199.95		0.03	0.0009
2	0.178	200.00		0.02	0.0004
3	0.178	199.98	199.98	0.00	0.0000
4	0.178	200.00		0.02	0.0004
5	0.175	199.95		0.03	0.0009

Standard deviation: 0.025; Confidence limit (at 99 %): 99.98 ± 0.047

TABLE-4
BINARY SEPARATION OF Pd(II) WITH 4-MBO IN BUTANOL FROM AQUEOUS MEDIA

Binary mixture metal (ppm)	Palladium found (ppm)	
	Present method	Standard method
Pd(5) + Cr(5)	4.99	5.01
Pd(6) + Zn(4)	4.90	3.99
Pd(4) + Pt(6)	5.45	5.99
Pd(6) + V(4)	4.00	4.01
Pd(5) + Zr(5)	4.95	5.01

TABLE-5
DETERMINATION OF Pd(II) FROM REAL SAMPLES

Standard samples	Palladium found (%)	
	Present method	DMG method
Silver Alloys	0.090	0.098
Pd-Charcoal catalyst	10.00	10.01
Pd-$BaSO_4$ catalyst	0.850	0.890
Pd-$CaCO_3$ catalyst	4.400	4.410

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